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(58) Field of search
C3J
(71) Applicants
Texaco Development
Corporation,
135 East 42nd Street,
New York, N.Y. 10017,
United States of America
(72) Inventors
James Oliver Waldbillig
Carmen Michael Cusano
(74) Agents
Michael Burnside &
Partners

(54) **Lubricating oil additives**

(57) This invention concerns an additive acting as dispersant and viscosity index improver for lubricating oils which is produced by reacting a polyamine containing both primary and tertiary amino groups (e.g. a dialkylaminoalkylamine or a primary-amino substituted cyclic amine) with a hydroperoxidized ethylene-propylene copolymer or terpolymer in the presence of a free radical initiator and air.

SPECIFICATION

Lubricating oil additives and composition containing same

The present invention relates to additives for lubricating oils used in internal combustion engines, and to lubricating compositions containing such additives.

The additives of the invention possess dispersancy and viscosity index improving properties; that is to say, they improve the viscosity properties of a lubricant by lessening its tendency to change viscosity as the temperature changes and, at the same time, disperse and maintain suspended solids, e.g. sludge and varnish, which form in the lubricant during use.

The prior art includes U.S. Patents No. 3,789,980; 3,687,849; 3,879,304 and 3,076,791. The first of these discloses a lubricating oil additive consisting of the reaction product of a primary or secondary amine, and a hydroxyperoxidized ethylene/propylene copolymer; U.S. Patent No. 3,687,849 describes lubricant additives consisting of graft polymers prepared from various polymerizable unsaturated monomers and an oxidized degraded interpolymers of ethylene and propylene. U.S. Patent No. 3,879,304 reports a terpolymer having a polymethacrylate grafted thereon. U.S. Patent No. 3,076,791 discloses lubricating oil additives produced by the free radical reaction of an ethylene/propylene copolymer with an amine.

The present invention provides an additive useful as a dispersant and viscosity index improver having a thickening power at 99°C in the range of 1.0 to 100 SUS and an infrared spectrum containing absorbance peaks at frequencies in the range of 1550-1750 cm^{-1} , which comprises the reaction product of a polyamine containing both tertiary amino and primary amino nitrogen groups, and a hydroperoxidized ethylene/propylene copolymer or terpolymer having a molecular weight of 5000 to 500,000, reacted at a temperature of 80 to 250°C under a pressure of 0.097 to 6.99 mPa (0 to 1000 psig) in the presence of a free radical initiator and air.

The present invention also provides a lubricant composition which comprises a major proportion of a lubricating oil and an effective dispersing and viscosity improving amount of an additive as defined above.

The hydroperoxidized polymer can be an ethylene propylene copolymer or a terpolymer of ethylene, propylene and a monomer which is an unsaturated hydrocarbon such as a diene, cycloalkene or bicycloalkene having a molecular weight in the range of 5,000 to 500,000. Examples of suitable types of polyamides include dialkylamino alkylamines such as dimethylaminopropylamine, diethylaminopropylamine, or dimethylaminoethylamine, and those in which the tertiary amino group exists in a ring system such as pyridine, piperidine, quinoline, quinoline or morpholine ring substituted with a group containing or comprising a primary amino group. Examples of such cyclic compounds include 2

- aminopyridine, 2 - piperidinoethylamine, 5 -

aminoquinoline, N - (3 - aminopropyl) - morpholine or 2 - aminopyrimidine.

The additives of the invention can be prepared by dissolving the ethylene/propylene polymer in an inert solvent at a temperature of around 70°C using agitation. A free radical initiator, such as azo - bis - isobutyronitrile, is added and air is bubbled through the reaction medium for 2 to 48 hours. A solvent, such as the lubricating oil whose properties are to be improved, is then added, and the inert solvent is removed by vacuum distillation. Next the amine is introduced into the reaction mass and the mixture is heated for 0.5 to 20 hours at 80 to 250°C preferably 130 to 190°C, under an atmosphere of nitrogen at a pressure of 0.097 to 6.99 mPa (0 to 1000 psig), preferably 0.131 to 0.441 mPa (5 to 50 psig).

The reaction mass again is distilled under vacuum at 80 to 300°C, to remove excess amine and catalyst residue. The additive can be precipitated by boiling in isopropyl alcohol, and filtered off. The proportions by weight of the starting materials can for example, be:

10 to 1000 parts by weight of ethylene/propylene copolymer or terpolymer,
1 to 20 parts by weight of free radical initiator,
100 to 100,000 parts by weight of inert solvent,
1 to 20 parts by weight of amine, and
100 to 100,000 parts by weight of oil.

The dispersant additives of the invention were tested for their effectiveness in mineral lubricating oil compositions in the dispersancy test, and in the Sequence V-C Test.

The dispersancy test is conducted by heating the test oil mixed with a synthetic hydrocarbon blowby and a diluent oil at a fixed temperature for a fixed time. After heating, the turbidity of the resultant mixture is measured. A low percentage turbidity (0-10) is indicative of good dispersancy, while high percentages (20-100) indicate oils of increasingly poor dispersancy.

The Sequence V-C Test is detailed in the ASTM Special Technical Publication under heading 310-F. The test is used to evaluate crankcase motor oils with respect to sludge and varnish deposits as well as their ability to keep the positive crankcase ventilation (PCV) valve clean and functioning properly. Ratings of 0 to 10 are given, 10 representing absolutely clean, and 0 rating representing heavy sludge and varnish deposits.

The rust inhibiting properties of the novel lubricants of the invention were determined in the SE required standard MS-IIC Rust Test. This test was developed and is effective for evaluating crankcase oils with respect to low temperature rusting.

Components used to formulate lubricating compositions containing the additives of the invention are identified below:

COMPONENT A:

IDENTITY: Dinonyldiphenylamine (mostly 4,4' - substituted)

COMPONENT B:

IDENTITY: 18:1 overbased calcium sulfonate in oil BB

COMPONENT C:

IDENTITY: Ethylene - propylene co-polymer of

20,000 to 50,000 molecular weight (13.0 wt. % in oil CC)

COMPONENT D:

IDENTITY: Polyester type methacrylate copolymer

COMPONENT E:

IDENTITY: Reaction product of sulfurized polybutene and tetraethylene pentamine

COMPONENT F:

IDENTITY: 50% reaction of polybutenyl succinimide (mol. wt. 1300) in oil "BB"

COMPONENT G:

IDENTITY: 10 to 20% hydroperoxidized dimethylaminopropylamine aminated ethylenep-

ropylene copolymer in 90 to 80% of oil "CC"

COMPONENT H:

IDENTITY: Zinc dialkyldithiophosphate

The base oil for the additives of the invention can be predominantly paraffinic or naphthenic, or it can be a mixture of both types of mineral oils. In general, the base oil will be a relatively highly refined mineral oil of predominantly paraffinic nature and will have a viscosity in the range of 30 to 100 Saybolt Universal Seconds (SUS) at 99°C.

Typical base oils used in the practice of the invention had the following inspection values:

Oil No.	Viscosity 38°C.	(SUS) 99°C.	Gravity	Pour Point °C.	%S
AA	127	41.5	0.8644	-20	0.16
BB	98	38.8	0.8844	-12	0.12
CC	99	39.1	0.8639	0	0.25
DD	332	53.2	0.8822	-20	0.40
EE	846	78.1	0.8927	-9	0.34
FF	333	53.3	0.8838	-12	0.29

The invention is further illustrated by the following Example:

EXAMPLE

Materials: 200 g amorphous copolymer of ethylene and propylene (EPSyn 5006), 8.0 Azo - bis - isobutyronitrile (AIBN), 200 ml. benzene, 4.0 g dimethylaminopropylamine (DMAPA), 1800 g Oil AA.

Procedure: The e-p copolymer used is sold by the Copolymer Rubber and Chemical Corporation under the name of "EPSyn 5006". The mole percent ethylene content of the polymer is between 60 and 63 and its molecular weight, as expressed by a Mooney viscosity, is nominally 50 ± 5 ML 1 + 8 a 121°C with a moisture content of less than 0.5%.

The EPSyn 5006 was dissolved in benzene at 70°C with stirring. The AIBN was added at 70°C and air was bubbled through the rapidly stirred solution at 400 ml/min for 18 hours. After adding Oil AA, the solution was stripped to 158°C (0.13 mm). The DMAPA was charged and the solution was heated

ten hours at 160°C. Stripping the product to 146°C (0.07 mm) yielded 2007 g of product (Z).

The sample was filtered through Super-Cel. The polymer, isolated by precipitation in boiling isopropyl alcohol, analyzed 0.10% N.

Test Data in Oil "AA"

Conc. of Z wt. % in Oil 5.0 10.0 15.0
Dispersancy Test 15.0 9.5 5.5
(standards: 3.0, 68, 57)

99°C. Thickening Power (SUS) — 8.8 —

The composition made above was tested in an engine test under similar conditions as a hydroperoxidized ethylene/propylene copolymer aminated with tetraethylene - pentamine and disclosed in U.S. Patent No. 3,785,980 (Y) and as a dispersant "X" consisting of a 41% tetrapolymer of butyl, dodecyl, octadecyl and N,N-dimethylaminoalkyl methacrylates in a molar ratio of 21:50:25:4.

The data are given below:

Blend Comp (wt. %)	I	II	III
Z	9.0	—	—
Y	—	9.0	—
X	—	—	9.0
Oil AA	74.1	74.1	79.10
Oil DD	10.0	10.0	10.0
Zinc Dialkyldithiophosphate	0.65	0.65	0.65
Overbased calcium sulfonate	1.0	1.0	1.0
Ethyl mono and dinonyldiphenylamine	0.25	0.25	0.25
13 wt. % copolymer ethylene/propylene (20,000-50,000 mol. wt.) (87% diluent oil CC)	5.0	5.0	—
Methyl silicone fluid (ppm)	150	150	—
Engine Rust Rating IIC Test	7.3	5.4	5.4

TABLE I

	Blend No.	IV Certified (SwRI)	V Screener	VI Screener	VII Screener	VIII Screener
5	Comp. wt. % Oil "AA"	75.81	73.37	80.39	79.19	Oil "EE" :22.82 Oil "FF" :65.00
10	"H"	1.36	1.38	1.36	1.36	1.36
	"A"	0.25	0.25	0.25	0.25	0.25
	"B"	1.48	1.50	1.50	1.50	1.51
	"C"	6.00	6.00	—	6.20	—
15	"D"	0.10	0.10	0.10	0.10	0.05
	"E"	—	2.40	—	—	—
	"F"	—	—	1.40	4.70	7.01
	"G"*	1.50	1.50	2.25	1.00	0.30
	<i>Dispersancy Test</i>					
20		2.5	2.5*	3.5	4.0	3.5
	Ref. Oils** FREO					
	126	2.5	2.5	2.5	2.5	2.5
	127	21.5	20.0	14.5	12.5	23.5
25	179	69.0	64.0	48.5	31.5	64.0
	VC Engine Test					
	Ave. Sludge	9.5	9.7	9.7	9.7	9.5
	Ave. Varnish	8.2	7.9	8.0	7.1	7.5
	Piston Skirt					
30	Varnish	7.0	7.9	8.0	7.2	8.1
	Oil Ring					
	Clogging	0	0	0	0	0
	Oil Screen					
	Clogging	0	0	0	0	0
35						

* The dispersancy was determined with a formulation containing 1.10% of component E.

** Concentration expressed on a "neat" polymer basis.

*** The FREO oils are Ford Motor Oils used for referencing the Seq. VC Engine Test.

The explanatory data given above show that the lubricating composition 1 containing the additive of the invention is superior to one containing a typical additive prepared by the method of U.S. Patent No. 3,785,980 (II), or a composition containing a methacrylate dispersant-VI improver (III).

Table I gives the results of V-C dispersancy test which have been conducted with the dimethylaminopropyl amine aminated - ethylene - propylene polymer (G).

As shown in the Table, "G" just barely failed (Avg. Varnish 7.9 vs. 8.0 for SE oil) the test with 2.40 wt % component "E" present as a supplementary dispersant (Blend No. V). In a formulation where 1.40 wt. % of component "F" was added as a supplementary dispersant, a passing SE quality oil was obtained (Blend VI).

Generally, the additives of this invention will be present in the finished composition to the extent of 0.5 to 30% by weight preferably 9 to 15% by weight. As indicated in the above Example, conventional lubricant additives, such as rust inhibitors and anti-oxidants can also be present.

While the proportions of constituents given in the foregoing description give outstanding dispersancy and viscosity improving characteristics with the given base oils, it will be appreciated that, by follow-

ing the teaching of the invention, those skilled in the art will be able without undue experimentation to determine optimum composition ranges for other oils.

It is to be understood that the foregoing specific examples are presented by way of illustration and explanation only that the invention is not limited by the details of such examples.

Thus, substantially similar results are obtained with additives prepared by the procedure of the Example and using, in the place of DMAPA, 2 - aminopyridine, 2 - piperidinoethyl amine, 5 - aminoquinoline, N - (3 - aminopropyl) - morpholine and 2 - aminopyrimidine.

CLAIMS

1. An additive useful as a dispersant and viscosity index improver having a thickening power at 99°C in the range of 1.0 to 100 SUS and an infrared spectrum containing absorbance peaks at frequencies in the range of 1550-1750 cm⁻¹, which comprises the reaction product of a polyamine containing both tertiary amino and primary amino nitrogen groups, and a hydroperoxidized ethylene/propylene copolymer or terpolymer having a molecular weight of 5000 to 500,000, reacted at a temperature of 80 to 250°C under a pressure of 0.097 to 6.99 mPa (0 to 1000 psig) in the presence of a free radical initiator and air.

2. An additive as claimed in Claim 1, wherein the polyamine is a dialkylaminoalkylamine.
3. An additive as claimed in Claim 1, wherein the polyamine is dimethylamino - propylamine.
4. An additive as claimed in any preceding Claim wherein the polyamine contains a primary amino group and a tertiary amino group in which the nitrogen is part of a ring system.
5. An additive as claimed in Claim 4, wherein the polyamine comprises a pyridine, piperidine, quinoline, pyrimidine or morpholine ring substituted with a group containing or comprising a primary amino group.
6. An additive as claimed in any preceding claim wherein the reaction temperature is 130 to 190°C and the pressure is 0.131 to 0.441 mPa (5 to 50 psig).
7. An additive as claimed in Claim 1 and substantially as hereinbefore described with reference to the Example.
8. A lubricating composition which comprises a major proportion of a lubricating oil and an effective dispersing and viscosity improving amount of an additive as claimed in any one of the preceding claims.
9. A composition as claimed in Claim 8 wherein the additive is present in the amount of 0.5 to 30% by weight based on said oil.
10. A composition as claimed in Claim 8 and substantially as hereinbefore described with reference to the Example.
4. A composition as claimed in any preceding Claim wherein the polyamine contains a primary amino group and a tertiary amino group in which the nitrogen is part of a ring system.
5. A composition as claimed in Claim 4, wherein the polyamine comprises a pyridine, piperidine, quinoline, pyrimidine or morpholine ring substituted with a group containing or comprising a primary amino group.
6. A composition as claimed in Claim 1, wherein said polyamine is dimethylamino - propylamine and the reaction temperature is 130 to 190°C under a pressure of 0.131 to 0.441 mPa (5 to 50 psig).
7. A composition as claimed in any preceding Claim, wherein said hydrocarbon is a diene, cycloalkene or a bicycloalkene.
8. A composition as claimed in any preceding Claim, wherein said additive is present in an amount of 0.5 to 30 percent of weight of said oil.
9. A composition as claimed in Claim 1 and substantially as hereinbefore described with reference to the Example.

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New claims or amendments to claims filed on
25/5/79 superseded all claims

35 New or amended claims:—

1. A lubricating composition which comprises a major portion of a lubricating oil and an effective dispersing and viscosity improving amount of an additive having a thickening power at 210°F in the range of 1.0 to 100 SUS and an infrared spectrum containing absorbance peaks at frequencies in the range of 1550-1750 cm⁻¹, obtained by dissolving in an inert solvent from 10 to 100,000 parts by weight of an ethylene/propylene copolymer or a terpolymer of ethylene, propylene an unsaturated hydrocarbon, said copolymer or terpolymer having a molecular weight of 5000 to 500,000; adding to the resulting solution a free radical initiator catalyst; bubbling air through the reaction medium to hydroperoxidize said copolymer or terpolymer; then adding from 100 to 100,000 parts of said lubricating oil; removing said inert solvent by distillation at reduced pressure; adding 1 to 20 parts by weight of a polyamine containing both tertiary and primary amino nitrogen groups; heating the mixture for 0.5 hours to 20 hours at a temperature of 80 to 250°C under a pressure of 0.097 to 6.99 mPa (0 to 1000 psig) and distilling the resulting reaction mass under reduced pressure at 80 to 300°C to remove excess polyamine and initiator.
2. A composition as claimed in Claim 1, wherein the polyamine is a dialkylaminoalkylamine.
3. A composition as claimed in Claim 1, wherein the polyamine is dimethylamino - propylamine.